DYES FOR KERATIN FIBERS, THE DYES CONTAINING N-BENZYL-P-PHENYLENEDIAMINE DERIVATIVES AND NOVEL N-BENZYL-P-PHENYLENEDIAMINE DERIVATIVES

The present invention relates to agents for oxidatively dyeing keratin fibers, especially human hair, on the basis of a combination of a developer and coupler, which contains N-benzyl-p-phenylenediamine derivatives as developer, as well as to new N-benzyl-p-phenylenediamine derivatives.

In the field of dyeing keratin fibers, especially of dyeing hair, oxidation dyes have achieved considerable importance. The dyeing results here from the reaction of certain developers with couplers in the presence of a suitable oxidizing agent. As developers, especially 2,5-diaminotoluene, 2,5-diaminophenylethyl alcohol, p-aminophenol and 1,4-diaminobenzene are used here, while as couplers, resorcinol, 4-chlororesorcinol, 1-naphthol, 3-aminophenol and derivatives of m-phenylenediamine, for example, are named.

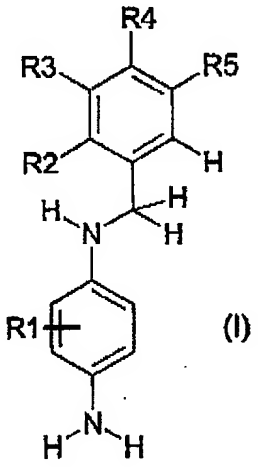
Oxidation dyes, which are used for dyeing human hair, must satisfy numerous requirements, in addition to dyeing in the desired intensity. For example, the dyes must be safe from a toxicological and dermatological point of view and the hair dyeings achieved must have good light fastness, permanent waving fastness, acid resistance and crocking fastness. In any case, such dyeings must remain stable for a period of at least 4 to 6 weeks without the action of light, rubbing and chemical agents. In addition, it is necessary that a broad range of different color nuances can be produced by combining suitable developers and couplers.

From the German Offenlegungsschrift 34 32 214, agents, which contain a particular N-benzyl-p-phenylenediamine, such as N-benzyl-p-phenylenediamine,

N4-benzyl-1,4-diamino-2-methylbenzene and 2-(((4-aminophenyl)amino)methyl)-4,6-dichloro-phenol, are already known for dyeing hair. However, these compounds do not fulfill the requirements, which must be met by dyes for oxidation dyes, in every respect. There is therefore a continuing need for further, suitable, new dyes.

It has now been found that, if N-benzyl-p-phenylenediamine derivatives of the general Formula (I) are used, intensive brown, blue and red color nuances are obtained.

The object of the present invention therefore is an agent for oxidatively dyeing keratin fibers, such as wool, fur, feathers or hair, especially human hair, on the basis of a combination of developer and coupler, which contains, as developer, at least one N-benzyl-p-phenylenediamine derivative of Formula (I),



(I)

in which

R1 R1 is hydrogen, a (C_1-C_4) alkyl group or a hydroxy-(C_1-C_4) alkyl group,

R2 is hydrogen, a halogen atom (F, Cl, Br, I), a cyano group, a (C_1-C_4) alkoxy group, a hydroxy (C_1-C_4) alkoxy group, a (C_1-C_6) alkyl group, a (C_1-C_4) alkyl thioether group, a mercapto group, a nitro group, an amino group, a (C_1-C_4) alkylamino group, a di-(C_1-C_4) alkylamino

group, a di-(hydroxy-(C_1-C_4)-alkyl) amino group, a (hydroxy-(C_1-C_4)-alkyl) amino group, a trifluoromethane group, a -$C(O)CH_3$ group, a -$C(O)CF_3$ group, an -$Si(CH_3)_3$ group, a hydroxy-(C_1-C_4) alkyl group, a dihydroxy-(C_3-C_4) alkyl group or a morpholino group

R3, R4 independently of one another are hydrogen, a halogen atom, a hydroxy group, a (C_1-C_4) alkoxy group, a hydroxy-(C_1-C_4) alkoxy group, a (C_1-C_6) alkyl group, a (C_1-C_4) alkyl thioether group, a mercapto group, an amino group, a (C_1-C_6) alkylamino group, a di-(C_1-C_6) alkylamino group, a di-(hydroxy-(C_1-C_4)-alkylamino group, a hydroxy-(C_1-C_4) alkylamino group, a trifluoromethane group, an acetamido group, a -$C(O)CH_3$ group, a -$C(O)CF_3$ group, an -$Si(CH_3)_3$ group, a hydroxy-(C_1-C_4) alkyl group or a dihydroxy-(C_3-C_4) alkyl group or R3 and R4 together form an -O-CH2-O- bridge and

R5 is hydrogen, a hydroxy group or a (C_1-C_6) alkyl group,

with the proviso that

(i) at least one of the R2 to R5 groups is different from a hydrogen and

(ii) R1 is not hydrogen or a (C1-C4) alkyl group when R2 = R4 = R5 = hydrogen and R3 = chlorine.

The following, for example, can be mentioned as examples of compounds of Formula (I): N-((2-aminophenyl)methyl)-1,4-diaminobenzene, N-((3-aminophenyl)-methyl)-1,4-diaminobenzene, N-((3-hydroxyphenyl)methyl)-1,4-diaminobenzene, N-((4-aminophenyl)methyl)-1,4-diaminobenzene, N-((4-hydroxyphenyl)methyl)-1,4-diaminobenzene, N-((2-(1-hydroxyethoxy)-phenyl)-methyl)-1,4-diaminobenzene, N-((2-methoxyphenyl)methyl)-1,4-diaminobenzene, N-((3-(1-hydroxyethoxy)-phenyl)methyl)-1,4-diaminobenzene, N-((3-methoxyphenyl)methyl)-1,4-diaminobenzene, N-((4-hydroxy-3,5-dimethyl-phenyl)methyl)-1,4-diaminobenzene, N-((4-(1-hydroxyethoxy)-phenyl)methyl)-1,4-diaminobenzene, N-((4-methoxyphenyl)methyl)-1,4-diaminobenzene, N-((2-(2-

hydroxyethylamino)-phenyl)methyl)-1,4-diaminobenzene, N-((2-(bis-(2-hydroxyethyl)amino)-phenyl)methyl)-1,4-diaminobenzene, N-((2-dimethylamino-phenyl)methyl)-1,4-diaminobenzene, N-((2-pyrrolidino-phenyl)methyl)-1,4-diaminobenzene, N-((3-(2-hydroxyethylamino)-phenyl)methyl)-1,4-diaminobenzene, N-((3-(bis-(2-hydroxyethyl)amino)-phenyl)methyl)-1,4-diaminobenzene, N-((3-dimethylaminophenyl)methyl)-1,4-diaminobenzene, N-((3-pyrrolidino-phenyl)methyl)-1,4-diaminobenzene, N-((4-(2-hydroxyethylamino)-phenyl)methyl)-1,4-diaminobenzene, N-((4-(bis-(2-hydroxyethyl)amino)-phenyl)methyl)-1,4-diaminobenzene, N-((4-dimethylamino-phenyl)methyl)-1,4-diaminobenzene, N-((4-pyrrolidino-phenyl)methyl)-1,4-diaminobenzene, N-benzo[1,3]dioxol-5-ylmethyl-1,4-diaminobenzene, N-benzo[1,3]dioxol-6-ylmethyl-1,4-diaminobenzene, N-{2-[(4-amino-phenylamino)-methyl]-phenyl}-acetamide, N-{3-[(4-amino-phenylamino)-methyl]-phenyl}-acetamide, N-{4-[(4-amino-phenylamino)-methyl]-phenyl}-acetamide, N-((2,3-diaminophenyl)methyl)-1,4-diaminobenzene, N-((2,3-dihydroxyphenyl)methyl)-1,4-diaminobenzene, N-((2,4-diaminophenyl)methyl)-1,4-diaminobenzene, N-((2,4-dihydroxyphenyl)methyl)-1,4-diaminobenzene, N-((2,5-diaminophenyl)methyl)-1,4-diaminobenzene, N-((2,5-dihydroxyphenyl)methyl)-1,4-diaminobenzene, N-((2,6-diaminophenyl)methyl)-1,4-diaminobenzene, N-((2,6-dihydroxyphenyl)methyl)-1,4-diaminobenzene, N-((2-hydroxy-3-aminophenyl)methyl)-1,4-diaminobenzene, N-((2-hydroxy-4-aminophenyl)methyl)-1,4-diaminobenzene, N-((2-hydroxy-5-aminophenyl)methyl)- 1,4-diaminobenzene, N-((3-hydroxy-4-aminophenyl)methyl)- 1,4-diaminobenzene, N-((3-hydroxy-5-aminophenyl)methyl)-1,4-diaminobenzene, N-((2-amino-3-hydroxyphenyl)methyl)-1,4-diaminobenzene, N-((2-amino-4-hydroxyphenyl)methyl)-1,4-diaminobenzene, N^1-((2-aminophenyl)methyl)-2-(2-hydroxyethyl)-1,4-diaminobenzene, N^1-((2-aminophenyl)methyl)-2-methyl-1,4-diaminobenzene, N^1-((3-aminophenyl)methyl)-2-(2-hydroxyethyl)-1,4-diaminobenzene, N^1-((3-aminophenyl)methyl)-2-methyl-1,4-diaminobenzene, N^1-((3-hydroxyphenyl)methyl)-2-(2-hydroxyethyl)-1,4-diaminobenzene, N^1-((3-hydroxyphenyl)methyl)-2-methyl-1,4-diaminobenzene, N^1-((4-aminophenyl)methyl)-2-(2-hydroxyethyl)-1,4-diaminobenzene, N^1-((4-

aminophenyl)methyl)-2-methyl-1,4-diaminobenzene, N^1-((4-hydroxyphenyl)methyl)-2-(2-hydroxyethyl)-1,4-diaminobenzene, N^1-((4-hydroxyphenyl)methyl)-2-methyl-1,4-diaminobenzene, N^4-((2-aminophenyl)methyl)-2-(2-hydroxyethyl)-1,4-diaminobenzene, N^4-((2-aminophenyl)methyl)-2-methyl-1,4-diaminobenzene, N^4-((3-aminophenyl)methyl)-2-(2-hydroxyethyl)-1,4-diaminobenzene, N^4-((3-aminophenyl)methyl)-2-methyl-1,4-diaminobenzene, N^4-((3-hydroxyphenyl)methyl)-2-(2-hydroxyethyl)-1,4-diaminobenzene, N^4-((3-hydroxyphenyl)methyl)-2-methyl-1,4-diaminobenzene, N^4-((4-aminophenyl)methyl)-2-(2-hydroxyethyl)-1,4-diaminobenzene, N^4-((4-aminophenyl)methyl)-2-methyl-1,4-diaminobenzene, N^4-((4-hydroxyphenyl)methyl)-2-(2-hydroxyethyl)-1,4-diaminobenzene, N^4-((4-hydroxyphenyl)methyl)-2-methyl-1,4-diaminobenzene.

Compounds of Formula (I) are preferred in which

(i) R1 and one of the groups R2 to R5 is hydrogen and/or

(ii) three of the R1 to R5 groups are hydrogen and the two remaining groups, independently of one another, represent hydrogen, a methoxy group, a hydroxy group or an amino group or, in the case of R3 and R4, jointly form an -O-CH2-O bridge, in which case R2 is not a hydroxy group and at least one of the R2 to R5 groups is not hydrogen.

The following N-benzyl-p-phenylenediamine derivatives of Formula (I) are particularly preferred: N-((3-hydroxyphenyl)methyl)-1,4-diaminobenzene; N-((4-aminophenyl)methyl)-1,4-diaminobenzene; N-((4-hydroxyphenyl)-methyl)-1,4-diaminobenzene; N-((2-methoxyphenyl)methyl)-1,4-diaminobenzene; N-((4-hydroxy-3,5-dimethyl-phenyl)methyl)-1,4-diaminobenzene; N-((4-(2-hydroxyethoxy)-phenyl)methyl)-1,4-diaminobenzene; N-benzo[1,3]dioxol-5-ylmethyl-1,4-diaminobenzene; N-{4-[(4-aminophenylamino)-methyl]-phenyl}-acetamide and N-((4-methoxyphenyl)-methyl)-1,4-diaminobenzene, as well as their physiologically compatible salts.

The compounds of Formula (I) can be used as free bases, as well as in the form of their physiologically compatible salts with inorganic or organic acids, such as hydrochloric acid, sulfuric acid, phosphoric acid, acetic acid, propionic acid, lactic acid or citric acid.

The N-benzyl-p-phenylenediamine derivatives of Formula (I) are contained in the inventive dyes in a total amount of about 0.005 to 20 percent by weight, amount of about 0.01 to 5 percent by weight and, in particular, of 0.1 to 2.5 percent by weight being preferred.

As coupler substances, preferably 2,6-diaminopyridine, 2-amino-4-[(2-hydroxyethyl)amino]-anisole, 2,4-diamino-1-fluoro-5-methylbenzene, 2,4-diamino-1-methoxy-5-methylbenzene, 2,4-diamino-1-ethoxy-5-methylbenzene, 2,4-diamino-1-(2-hydroxyethoxy)-5-methylbenzene, 2,4-di[(2-hydroxyethyl)amino]-1,5-dimethoxybenzene, 2,3-diamino-6-methoxy-pyridine, 3-amino-6-methoxy-2-(methylamino)-pyridine, 2,6-diamino-3,5-dimethoxy-pyridine, 3,5-diamino-2,6-dimethoxy-pyridine, 1,3-diaminobenzene, 2,4-diamino-1-(2-hydroxyethoxy)-benzene, 2,4-diamino-1,5-di(2-hydroxyethoxy)-benzene, 1-(2-aminoethoxy)-2,4-diaminobenzene, 2-amino-1-(2-hydroxyethoxy)-4-methylaminobenzene, 2,4-diaminophenoxyacetic acid, 3-[di(2-hydroxyethyl)amino]-aniline, 4-amino-2-di[(2-hydroxyethyl)amino]-1-ethoxybenzene, 5-methyl-2-(1-methylethyl)-phenol, 3-[(2-hydroxyethyl)amino]-aniline, 3-[(2-aminoethyl)-amino]-aniline, 1,3-di(2,4-diaminophenoxy)-propane, di(2,4-diaminophenoxy)-methane, 1,3-diamino-2,4-dimethoxybenzene, 2,6-bis(2-hydroxyethyl)amino toluene, 4-hydroxyindole, 3-dimethylaminophenol, 3-diethylaminophenol, 5-amino-2-methylphenol, 5-amino-4-fluoro-2-methylphenol, 5-amino-4-methoxy-2-methylphenol, 5-amino-4-ethoxy-2-methylphenol, 3-amino-2,4-dichlorophenol, 5-amino-2,4-dichlorophenol, 3-amino-2-methylphenol, 3-amino-2-chloro-6-methylphenol, 3-aminophenol, 2-[(3-hydroxyphenyl)amino]-acetamide, 5-[(2-hydroxyethyl)amino]-2-methylphenol, 3-[(2-hydroxyethyl)amino]-phenol, 3-[(2-methoxyethyl)-amino]-phenol, 5-amino-2-

ethylphenol, 2-(4-amino-2-hydroxyphenoxy)-ethanol, 5-[(3-hydroxypropyl)amino]-2-methylphenol, 3-[(2,3-dihydroxypropyl)amino]-2-methylphenol, 3-[(2-hydroxyethyl)amino]-2-methylphenol, 2-amino-3-hydroxy-pyridine, 5-amino-4-chloro-2-methylphenol, 1-naphthol, 1,5-dihydroxy-naphthalene, 1,7-dihydroxy-naphthalene, 2,3-dihydroxy-naphthalene, 2,7-dihydroxy-naphthalene, 2-methyl-1-naphthol acetate, 1,3-dihydroxybenzene, 1-chloro-2,4-dihydroxybenzene, 2-chloro-1,3-dihydroxybenzene, 1,2-dichloro-3,5-dihydroxy-4-methylbenzene, 1,5-dichloro-2,4-dihydroxybenzene, 1,3-dihydroxy-2-methylbenzene, 3,4-methylenedioxy-phenol, 3,4-methylenedioxy-aniline, 5-[(2-hydroxyethyl)amino]-1,3-benzodioxol, 6-bromo-1-hydroxy-3,4-methylenedioxy-benzene, 3,4-diamino-benzoic acid, 3,4-dihydro-6-hydroxy-1,4(2H)-benzoxazine, 6-amino-3,4-dihydro-1,4(2H)-benzoxazine, 3-methyl-1-phenyl-5-pyrazolone, 5,6-dihydroxy-indole, 5,6-dihydroxy-indoline, 5-hydroxy-indole, 6-hydroxy-indole, 7-hydroxy-indole and 2,3-indolinedione come into consideration.

Although the advantageous properties of the compounds of formula (I) described here suggest that these be used as the only developer, it is, of course, also possible to use these compounds together with known developers, such as 1,4-diaminobenzene, 2,5-diaminotoluene, 2,5-diaminophenylethanol, 4-aminophenol and its derivatives (for example, 4-amino-3-methylphenol), 4,5-diamino-1-benzyl-1H-pyrazole, 4,5-diamino-1-((4'-methylbenzyl)-1H-pyrazole, 4,5-diamino-1H-pyrazole, 4,5-diamino-1-(4'-methoxybenzyl)-1H-pyrazole, 4,5-diamino-1-(3'-methoxybenzyl)-1H-pyrazole, 4,5-diamino-1-(4'-chlorobenzyl)-1H-pyrazole, 4,5-diamino-1-((4'-methylphenyl)-1H-pyrazole, 4,5-diamino-1-(4'-methoxyphenyl)-1H-pyrazole, 4,5-diamino-1-(3'-methoxyphenyl)-1H-pyrazole, 4,5-diamino-1-(4'-chlorophenyl)-1H-pyrazole, 4,5-diamino-1-(2'-hydroxyethyl)-1H-pyrazole, 4,5-diamino-1-methyl-1H-pyrazole, 4,5-diamino-1-ethyl-1H-pyrazole, 4-amino-1-((4-methoxyphenyl)methyl)-5-(methylamino)-1H-pyrazole, 4-amino-5-((2-hydroxyethyl)amino)-1-(phenylmethyl)-1H-pyrazole, 4,5-diamino-1-methyl-3-phenyl-1H-pyrazole, 4,5-diamino-1-(2-hydroxyethyl)-3-phenyl-1H-pyrazole, 4,5-diamino-1,3-dimethyl-1H-

pyrazole, 4,5-diamino-3-methyl-1-phenyl-1H-pyrazole, 4,5-diamino-1-(1-isopropyl)-1H-pyrazole or tetraaminopyrimidines.

The couplers and the developers may be contained in the inventive dyes in each case individually or in admixture with one another, the total amount of the couplers and the developers in the inventive dye (based on the total amount of the dye) in each case being about 0.005 to 20 percent by weight, preferably about 0.01 to 5.0 percent by weight and particularly 0.1 to 2.5 percent by weight. The total amount of the combination of developer and coupler in the dye described here preferably is about 0.01 to 20 percent by weight, an amount of about 0.02 to 6 percent by weight and especially of 0.2 to 10 percent by weight being particularly preferred. The developers and couplers generally are used in approximately equimolar amounts; in this connection, however, it is not disadvantageous if the developers or the couplers are present in a certain excess (such as a ratio of coupler to developer of 1 : 2 to 1 : 0.5).

Furthermore, the inventive dye may additionally contain other dye components, such as 6-amino-2-methylphenol and 2-amino-5-methylphenol, as well as conventional direct dyes, for example, triphenylmethane dyes such as 4-[(4'-aminophenyl)-(4'-imino-2",5"-cyclohexadiene-1"-ylidene)-methyl]-2-methylaminobenzene monohydrochloride (C.I. 42 510) and 4-[(4'-amino-3'-methyl-phenyl)-(4"-imino-3"-methyl-2",5"-cyclohexadiene-1"-ylidene)-methyl]-2-methylaminobenzene monohydrochloride (C.I. 42 520), aromatic nitro dyes such as 4-(2'-hydroxyethyl)amino-nitrotoluene, 2-amino-4,6-dinitrophenol, 2-amino-5-(2'-hydroxyethyl)amino-nitrobenzene, 2-chloro-6-(ethylamino)-4-nitrophenol, 4-chloro-N-(2-hydroxyethyl)-2-nitroaniline, 5-chloro-2-hydroxy-4-nitroaniline, 2-amino-4-chloro-6-nitrophenol and 1-[(2'-ureidoethyl)amino-4-nitrobenzene, azo dyes such as the sodium salt of 6-[(4'-aminophenyl)azo]-5-hydroxy-naphthalene-1-sulfonic acid (C.I. 14 805) and dispersion dyes such as, for example, 1,4-diaminoanthraquinone and

1,4,5,8-tetraaminoanthraquinone. The aforementioned dye components may be contained in the inventive dyes in an amount of about 0.1 to 4 percent by weight.

Of course, if the couplers and developers as well as the other dye components are bases, they may also be used in the form of their physiologically compatible salts with organic or inorganic assets, such as hydrochloric acid or sulfuric acid, or, if they have aromatic OH groups, in the form of the salts with bases, such as alkali phenolates.

Moreover, the inventive dyes, if they are to be used to dye hair, may also contain other additives, conventionally used in cosmetic materials, for example, antioxidants, such as ascorbic acid, thioglycolic acid or sodium sulfite, as well as perfume oils, complexing agents, wetting agents, emulsifiers, thickeners and care materials.

The inventive dyes may be prepared in the form of a solution, especially an aqueous or aqueous alcoholic solution. However, the especially preferred form of the preparation is a cream, a gel or an emulsion. Its composition represents a mixture of the dye components with additives, which are usually employed for such preparations.

Conventional additives for solutions, creams, emulsions or gels are, for example, solvents such as water, low molecular weight aliphatic alcohols, such as ethanol, propanol or isopropanol, glycerin or glycols, such as 1,2-propylene glycol, wetting agents or emulsifiers of the anionic, cationic, amphoteric or nonionic class of surface active substances, such as fatty alcohol sulfates, ethoxylated fatty alcohol sulfates, alkyl sulfonates, alkylbenzene sulfonates, alkyltrimethylammonium salts, alkylbetaines, ethoxylated fatty alcohols, ethoxylated nonylphenoles, fatty acid alkanolamides and ethoxylated fatty acid esters, furthermore, thickeners such as higher molecular weight fatty alcohols, starch, cellulose derivatives, petroleum jelly,

paraffin oil and fatty acids, as well as care materials, such as cationic resins, lanolin derivatives, cholesterol, pantothenic acid and betaine. The components mentioned are used in amounts, which a customary for such purposes; for example, the wetting agents and emulsifiers are used in concentrations of about 0.5 to 30 percent by weight, the thickness in an amount of about 0.1 to 25 percent by weight and the care materials in a concentration of about 0.1 to 5 percent by weight.

Depending on the composition, the inventive dye may be slightly acidic, neutral or alkaline. In particular, it has a pH of 6.5 to 11.5, the adjustment to a basic pH preferably being made with ammonia. However, organic amines, such as monoethanolamine and triethanolamine, or also inorganic bases, such as sodium hydroxide and potassium hydroxide may also be used. For adjusting the pH in the acidic range, inorganic organic acids, such as phosphoric acid, acetic acid, citric acid or tartaric acid comes into consideration

If they are to be used for the oxidative dyeing of hair, the dyes, described above, are mixed immediately before use with an oxidizing agent and an amount of dye, sufficient for the treatment, is applied on the hair. Generally, about 50 to 200 gram of this mixture is applied, depending on the fullness of the latter. The ready-for-use oxidation dye, obtained upon mixing with the oxidizing agent, preferably has a pH of 6.5 to 11.5.

The following come into consideration as oxidizing agents for developing the hair dyeing: mainly hydrogen peroxide or its addition compounds with urea, melamine, sodium borate or sodium carbonate in the form of a 3 percent to 12 percent and preferably a 6 percent aqueous solution, also oxygen from the air. If a 6 percent hydrogen peroxide solution is used as oxidizing agent, the ratio by weight of hair dyeing agent to oxidizing agent is 5 : 1 to 1 : 2 and preferably 1 : 1. Larger amounts of oxidizing agent are used especially for higher concentrations of dye in the hair-dyeing agent or if greater bleaching of the hair is intended at the same time. The

mixture is allowed to act on the hair for about 10 to 45 minutes and preferably for 30 minutes at 15° to 50°C. The hair is then rinsed with water and dried. Optionally, after the rinsing, the hair is washed with a shampoo and possibly rinsed with a weak organic acid, such as citric acid or tartaric acid. Subsequently, the hair is dried.

The inventive dye, containing N-benzyl-p-phenylenediamine derivatives of Formula (I) as developer, makes dyeings possible with excellent color fastness, especially as far as light fastness, wash fastness and crock fastness are concerned. With regard to the color properties, the inventive dyeing agent offers a wide range of different color nuances, ranging from blond, brown, purple and violet to blue and black color shades, depending on the nature and composition of the dye components. The shades of color are distinguished here especially by their color intensity. The very good dyeing properties of the dye of the present invention are furthermore shown by the fact that this material enables even grayish hair, which has not previously been damaged chemically, to be dyed without problems and with good covering power.

The inventive N-benzyl-p-phenylenediamine derivatives of Formula (I) can be synthesized using known methods, such as the methods described in the examples.

The N-benzyl-p-phenylenediamine derivatives of Formula (I) are readily soluble in water and make dyeings possible with a high color intensity and excellent color fastness, especially as far as light fastness, wash fastness and crock fastness are concerned. They furthermore have an excellent shelf life, especially as a component of the oxidation dyes, which are described here.

A further object of the present invention are new N-benzyl-p-phenylenediamine derivatives of Formula (I), in which R4 is not a nitro group, a methyl group, a hydroxy group, an amino group, a dimethylamino group, a bromine

atom or a chlorine atom, when R1 = R2 = R3 = R5 = hydrogen, or their physiologically compatible, water-soluble salts.

The following examples are intended to explain the object of the invention in greater detail, without limiting the invention to these examples.

Examples

Example 1: Synthesis of N-benzyl-1,4-diaminobenzenes

t-Butyl N-(4-aminophenyl) carbamate (0.031 gram, 0.15 mmoles) and 0.10 mmoles of the appropriate aldehyde are dissolved in 1,2-dichloroethane. Subsequently, 0.1 mL of an acetic acid solution (1 molar in 1,2-dichloroethane) and 0.06 g of $NaBH(OAc)_3$ (0.3 mmoles) are added and the reaction mixture is stirred for 5 to 15 hours at room temperature (20° to 25°C). At the end of the reaction, the reaction mixture is poured into 10 mL of ethyl acetate and the organic phase is extracted with sodium hydrogen carbonate and then dried with magnesium sulfate. The solvent is evaporated in a rotary evaporator and the residue purified on silica gel with petroleum ether/ethyl acetate (9 : 1). The product, so obtained, is heated to 50°C in 4 mL of ethanol and 1.5 mL of a2.9 molar ethanolic hydrochloric acid solution. The precipitate is filtered off, washed twice with 1 mL of ethanol and then dried.

a. N-((3-hydroxyphenyl)methyl)-1,4-diaminobenzene hydrochloride

Aldehyde used: 3-hydroxy-benzaldehyde

Yield: 0.025 g (87% of the theoretical)

Mass spectrum: MH+ 215(100)

b. N-((4-(2-hydroxyethoxy)-phenyl)methyl)-1,4-diaminobenzene hydrochloride

Aldehyde used: 4-(2-hydroxyethoxy)-benzaldehyde

Yield: 0.025 g (75% of the theoretical)

Mass spectrum: MH+ 259(100)

c. N-{4-[(4-aminophenylamino)-methyl]-phenyl}-acetamide hydrochloride

Aldehyde used: 4-acetamino-benzaldehyde

Yield: 0.025 g (76% of the theoretical)

Mass spectrum: MH+ 256(100)

d. 4-[(4-amino-phenylamino)-methyl]-2,6-dimethyl-phenol hydrochloride

Aldehyde used: 2,6-dimethyl-4-hydroxy-benzaldehyde

Yield: 0.025 g (79% of the theoretical)

Mass spectrum: MH+ 243(100)

e. N-benzo[1,3]dioxol-5-ylmethyl-1,4-diamino-benzene hydrochloride

Aldehyde used: 3,4-methylenedioxy-benzaldehyde

Yield: 0.025 g (79% of the theoretical)

Mass spectrum: MH+ 316(100)

f. N-((4-hydroxyphenyl)-methyl)-1,4-diaminobenzene

Aldehyde used: 4-hydroxy-benzaldehyde

Yield: 0.025 g (100% of the theoretical)

Mass spectrum: MH+ 215(100)

g. N-((4-aminophenyl)-methyl)-1,4-diaminobenzene hydrochloride

Aldehyde used: t-butyl N-(4-formyl-phenyl)carbamate

Yield: 0.025 g (77% of the theoretical)

Mass spectrum: MH+ 214(100)

h. N-(2-amino benzyl)-1,4-diaminobenzene hydrochloride

Aldehyde used: 2-amino-benzaldehyde

Yield: 0.025 g (77% of the theoretical)

Mass spectrum: MH+ 214(100)

i. N-(2-methoxy-benzyl)-1,4-diaminobenzene hydrochloride

Aldehyde used: 2-methoxy-benzaldehyde

Yield: 0.025 g (83% of the theoretical)

Mass spectrum: MH+ 229(100)

j. 4-[(4-aminophenylamino)-methyl]-1,2-dihydroxybenzene hydrochloride

Aldehyde used: 3,4-dihydroxy-benzaldehyde

Yield: 0.025 g (82% of the theoretical)

Mass spectrum: MH+ 231(100)

k. 5-[(4-aminophenylamino)-methyl]-1,3-dihydroxybenzene hydrochloride

Aldehyde used: 3,5-dihydroxy-benzaldehyde

Yield: 0.025 g (82% of the theoretical)

Mass spectrum: MH+ 231(100)

l. 5-(4-aminophenyl)aminomethyl-1,3-diaminobenzene hydrochloride

Aldehyde used: 3,5-diamino-benzaldehyde

Yield: 0.025 g (66% of the theoretical)

Mass spectrum: MH+ 228(100)

m. N-((4-methoxyphenyl)methyl)-1,4-diaminobenzene hydrochloride

Aldehyde used: 4-methoxy-benzaldehyde

Yield: 0.025 g (83% of the theoretical)

Mass spectrum: MH+ 229(100)

n. 4-amino-2-[(4-amino-phenylamino)-methyl]-phenol hydrochloride

Aldehyde used: t-butyl N-(4-hydroxy-3-formyl-phenyl)-carbamate

Yield: 0.025 g (73% of the theoretical)

Mass spectrum: MH+ 230(100)

o. N-(4-pyrrolidine-1-yl-benzyl)-1,4-diaminobenzene

Aldehyde used: 4-pyrrolidino-benzaldehyde

Yield: 10 g (30% of the theoretical)

p. 2-[{4-[(4-amino-phenylamino)-methyl]-phenyl}-(2-hydroxyethyl)-amino]-ethanol hydrochloride

Aldehyde used: 4-(bis(2-hydroxyethyl)amino)-benzaldehyde

Yield: 0.025 g (60% of the theoretical)

q. N-(4-nitro-benzyl)-1,4-diaminobenzene hydrochloride

Aldehyde used: 4-nitro-benzaldehyde

Yield: 0.025 g (79% of the theoretical)

Mass spectrum: MH+ 244(20)

r. N-(4-dimethylamino-benzyl)-1,4-diaminobenzene

Aldehyde used: 4-dimethylamino-benzaldehyde

Yield: 0.025 g (100% of the theoretical)

Mass spectrum: MH+ 242(25)

s. 2-[(4-amino-phenylamino)-methyl]1,4-dihydroxybenzene hydrochloride

Aldehyde used: 3,6-dihydroxy-benzaldehyde

Yield: 0.025 g (82% of the theoretical)

Mass spectrum: MH+ 231(100)

t. N-(2,4-dinitro-benzyl)-1,4-diaminobenzene hydrochloride

Aldehyde used: 2,4-dinitro-benzaldehyde

Yield: 0.025 g (69% of the theoretical)

Mass spectrum: MH+ 289(70)

u. N-(2-morpholino-4-yl-benzyl)-1,4-diaminobenzene hydrochloride

Aldehyde used: 2-morpholino-benzaldehyde

Yield: 0.025 g (70% of the theoretical)

Example 2: Synthesis of N^1-benzyl-1,4-diamino-2-methyl-benzenes and N^4-benzyl-1,4-diamino-2-methyl-benzenes

A mixture of 0.033 g (0.15 mmoles) of t-butyl N-(4-amino-2-methyl-phenyl) carbamate and t-butyl N-(4-amino-3-methyl-phenyl) carbamate and 0.1 mmoles of the appropriate aldehyde is dissolved in 1,2-dichloroethane. Subsequently, 0.1 mL of an acetic acid solution (1 molar in 1,2-dichloroethane) and 0.06 g of $NaBH(OAc)_3$ (0.3 mmoles) are added and the reaction mixture is stirred for 5 to 15 hours at room temperature (20° to 25°C). At the end of the reaction, the reaction mixture is poured into 10 mL of ethyl acetate and the organic phase is extracted with sodium hydrogen carbonate and then dried with magnesium sulfate. The solvent is evaporated in a rotary evaporator and the residue purified on silica gel with petroleum ether/ethyl acetate (9 : 1). The product, so obtained, is heated to 50°C in 4 mL of ethanol and 1.5 mL of a2.9 molar ethanolic hydrochloric acid solution. The precipitate is filtered off, washed twice with 1 mL of ethanol and then dried.

a. N^1-(4-amino-benzyl)-2-methyl-1,4-diaminobenzene hydrochloride and N^1-(4-amino-benzyl)-3-methyl-1,4-diaminobenzene hydrochloride

Aldehyde used: t-butyl N-(4-formyl-phenyl)-carbamate

Yield: 0.025 g (37% of the theoretical)

Mass spectrum: MH+ 228(40)

b. 4-amino-2-[(4-amino-2-methyl-phenylamino)-methyl]-phenol hydrochloride and 4-amino-2-[(4-amino-3-methyl-phenylamino)-methyl]-phenol hydrochloride

Aldehyde used: t-butyl N-(4-hydroxy-3-formyl-phenyl)-carbamate

Yield: 0.025 g (35% of the theoretical)

Mass spectrum: MH+ 244(100)

c. N^1-(2-methoxy-benzyl)-2-methyl-1,4-diaminobenzene hydrochloride and N^1-(2-methoxy-benzyl)-3-methyl-1,4-diaminobenzene hydrochloride

Aldehyde used: 2-methoxy-benzaldehyde

Yield: 0.025 g (39% of the theoretical)

Mass spectrum: MH+ 243(100)

d. N^1-(3-amino-benzyl)-2-methyl-1,4-diaminobenzene hydrochloride and N^1-(3-amino-benzyl)-3-methyl-1,4-diaminobenzene hydrochloride

Aldehyde used: 3-amino-benzaldehyde

Yield: 0.025 g (37% of the theoretical)

Mass spectrum: MH+ 228(100)

e. 3-[(4-amino-2-methyl-phenylamino)-methyl]-phenol hydrochloride and 3-[(4-amino-3-methyl-phenylamino)-methyl]-phenol hydrochloride

Aldehyde used: 3-hydroxybenzaldehyde

Yield: 0.025 g (41% of the theoretical)

Mass spectrum: MH+ 229(100)

f. N^1-(4-methoxy-benzyl)-2-methyl-1,4-diaminobenzene and N^1-(4-methoxy-benzyl)-3-methyl-1,4-diaminobenzene hydrochloride

Aldehyde used: 4-methoxy-benzaldehyde

Yield: 0.025 g (39% of the theoretical)

Mass spectrum: MH+ 243(100)

g. 5-(4-amino-2-methyl-phenyl)aminomethyl-1,3-diaminobenzene hydrochloride and 5-(4-amino-3-methyl-phenyl)aminomethyl-1,3-diaminobenzene hydrochloride

Aldehyde used: 3,5-diaminobenzaldehyde

Yield: 0.025 g (32% of the theoretical)

Mass spectrum: MH+ 243(100)

h. 2-{4-[(4-amino-2-methyl-phenylamino)-methyl]-phenoxy}-ethanol hydrochloride and 2-{4-[(4-amino-3-methyl-phenylamino)-methyl]-phenoxy}-ethanol hydrochloride

Aldehyde used: 4-(2-hydroxyethoxy)-benzaldehyde

Yield: 0.025 g (36% of the theoretical)

Mass spectrum: MH+ 273(100)

i. 2-[{4-[(4-amino-2-methyl-phenylamino)-methyl]-phenyl}-(2-hydroxyethyl)-amino]-ethanol and 2-[{4-[(4-amino-3-methyl-phenylamino)-methyl]-phenyl}-(2-hydroxyethyl)-amino]-ethanol

Aldehyde used: 4-(bis-(2-hydroxyethyl)-amino)-benzaldehyde

Yield: 10 g (16% of the theoretical)

j. N^1-(2-amino-benzyl)-2-methyl-1,4-diaminobenzene hydrochloride and N^1-(2-amino-benzyl)-3-methyl-1,4-diaminobenzene hydrochloride

Aldehyde used: 2-amino-benzaldehyde

Yield: 0.025 g (37% of the theoretical)

k. 2-[(4-amino-2-methyl-phenylamino)-methyl]-1,4-dihydroxybenzene hydrochloride and 2-[(4-amino-3-methyl-phenylamino)-methyl]-1,4-dihydroxybenzene hydrochloride

Aldehyde used: 3,6-dihydroxybenzaldehyde

Yield: 0.025 g (39% of the theoretical)

Mass spectrum: MH+ 245(100)

l. 2-methyl-N^1-(4-nitro-benzyl)-1,4-diaminobenzene hydrochloride and 3-methyl-N^1-(4-nitro-benzyl)-1,4-diaminobenzene hydrochloride

Aldehyde used: 4-nitro-benzaldehyde

Yield: 0.025 g (37% of the theoretical)

Mass spectrum: MH+ 258(100)

m. 2-{4-[(4-amino-2-methyl-phenylamino)-methyl]-phenoxy}-ethanol hydrochloride and 2-{4-[(4-amino-3-methyl-phenylamino)-methyl]-phenoxy}-ethanol hydrochloride

Aldehyde used: 4-(2-hydroxy-ethoxy)-benzaldehyde

Yield: 0.025 g (36% of the theoretical)

Mass spectrum: MH+ 273(100)

n. N-{4-[(4-amino-2-methyl-phenylamino)-methyl]-phenyl}-acetamide hydrochloride and N-{4-[(4-amino-3-methyl-phenylamino)-methyl]-phenyl}-acetamide hydrochloride

Aldehyde used: 4-acetamido-benzaldehyde

Yield: 0.025 g (36% of the theoretical)

Mass spectrum: MH+ 270(100)

o. 4-[(4-amino-2-methyl-phenylamino)-methyl]-phenol hydrochloride and 4-[(4-amino-3-methyl-phenylamino)-methyl]-phenol hydrochloride

Aldehyde used: 4-hydroxy-benzaldehyde

Yield: 0.025 g (41% of the theoretical)

Mass spectrum: MH+ 229(100)

p. 2-methyl-N^1-(2-morpholine-4-yl-benzyl)-1,4-diaminobenzene hydrochloride and 3-methyl-N^1-(2-morpholine-4-yl-benzyl)-1,4-diaminobenzene hydrochloride

Aldehyde used: 2-morpholino-benzaldehyde

Yield: 0.025 g (30% of the theoretical)

q. N^1-(4-dimethylamino-benzyl)-2-methyl-1,4-diaminobenzene and N^1-(4-dimethylamino-benzyl)-3-methyl-1,4-diaminobenzene

Aldehyde used: 4-dimethylamino-benzaldehyde

Yield: 0.025 g (48% of the theoretical)

Mass spectrum: MH- 254(100)

Example 3: Synthesis of N^1-benzyl-1,4-diamino-2-(2-hydroxyethyl)-benzenes and N^4-benzyl-1,4-diamino-2-(2-hydroxyethyl)benzenes

A mixture of 0.038 g (0.15 mmoles) of t-butyl N-(4-amino-2(2-hydroxyethyl)-phenyl) carbamate and N-(4-amino-3-(2-hydroxyethyl)-phenyl) carbamate and 0.1 mmoles of the appropriate aldehyde are dissolved in 1,2-dichloroethane. Subsequently, 0.1 mL of an acetic acid solution (1 molar in 1,2-dichloroethane) and 0.06 g of $NaBH(OAc)_3$ (0.3 mmoles) are added and the reaction mixture is stirred for 5 to 15 hours at room temperature (20° to 25°C). At the end of the reaction, the reaction mixture is poured into 10 mL of ethyl acetate and the organic phase is extracted with sodium hydrogen carbonate and then dried with magnesium sulfate. The solvent is evaporated in a rotary evaporator and the residue purified on silica gel with petroleum ether/ethyl acetate (9 : 1). The product, so obtained, is heated to 50°C in 4 mL of ethanol and 1.5 mL of a2.9 molar ethanolic hydrochloric acid solution. The precipitate is filtered off, washed twice with 1 mL of ethanol and then dried.

a. 2-[5-amino-2-(4-nitro-benzylamino)-phenyl]-ethanol hydrochloride and 2-[6-amino-3-(4-nitro-benzylamino)-phenyl]-ethanol hydrochloride

Aldehyde used: 4-nitro-benzaldehyde

Yield: 0.025 g (34% of the theoretical)

Mass spectrum: MH+ 288(100)

b. 2-[5-amino-2-(3-amino-benzylamino)-phenyl]-ethanol hydrochloride and 2-[6-amino-3-(3-amino-benzylamino)-phenyl]-ethanol hydrochloride

Aldehyde used: 3-amino-benzaldehyde

Yield: 0.025 g (34% of the theoretical)

Mass spectrum: MH+ 258(100)

c. 2-[5-amino-2-(4-amino-benzylamino)-phenyl]-ethanol hydrochloride and 2-[6-amino-3-(4-amino-benzylamino)-phenyl]-ethanol hydrochloride

Aldehyde used: t-butyl N-(4-formyl-phenyl)-carbamate

Yield: 0.025 g (34% of the theoretical)

Mass spectrum: MH+ 258(50)

d. 2-[5-amino-2-(4-methoxy-benzylamino)-phenyl]-ethanol hydrochloride and 2-[6-amino-3-(4-methoxy-benzylamino)-phenyl]-ethanol hydrochloride

Aldehyde used: 4-methoxy-benzaldehyde

Yield: 0.025 g (35% of the theoretical)

Mass spectrum: MH+ 273(100)

e. 2-[(4-{[4-amino-2-(2-hydroxyethyl)-phenylamino]-methyl}-phenyl)-(2-hydroxyethyl)-amino]-ethanol and 2-[(4-{[4-amino-3-(2-hydroxyethyl)-phenylamino]-methyl}-phenyl)-(2-hydroxyethyl)-amino]-ethanol

Aldehyde used: 4-bis(2-hydroxyethyl)amino-benzaldehyde

Yield: 15 g (25% of the theoretical)

f. 2-[5-amino-2-(2-methoxy-benzylamino)-phenyl]-ethanol hydrochloride and 2-[6-amino-3-(2-methoxy-benzylamino)-phenyl]-ethanol hydrochloride

Aldehyde used: 2-methoxy-benzaldehyde

Yield: 0.025 g (36% of the theoretical)

Mass spectrum: MH+ 273(100)

g. 2-[5-amino-2-(2-amino-benzylamino)-phenyl]-ethanol hydrochloride and 2-[6-amino-3-(2-amino-benzylamino)-phenyl]-ethanol hydrochloride

Aldehyde used: 2-amino-benzaldehyde

Yield: 0.025 g (34% of the theoretical)

Mass spectrum: MH+ 258(100)

h. 2-{[4-amino-2-(2-hydroxyethyl)-phenylamino]-methyl}-1,4-dihydroxy-benzene hydrochloride and 2-{[4-amino-3-(2-hydroxyethyl)-phenylamino]-methyl}-1,4-dihydroxy-benzene hydrochloride

Aldehyde used: 3,6-dihydroxy-benzaldehyde

Yield: 0.025 g (36% of the theoretical)

Mass spectrum: MH+ 275(100)

i. 4-amino-2-{[4-amino-2-(2-hydroxyethyl)-phenylamino]-methyl}-phenol hydrochloride and 4-amino-2-{[4-amino-3-(2-hydroxyethyl)-phenylamino]-methyl}-phenol hydrochloride

Aldehyde used: t-butyl N-(4-hydroxy-3-formyl-phenyl)-carbamate

Yield: 0.025 g (32% of the theoretical)

Mass spectrum: MH+ 274(100)

j. 2-[5-amino-2-(2-morpholine-4-yl-benzylamino)-phenyl]-ethanol hydrochloride and 2-[6-amino-3-(2-morpholine-4-yl-benzylamino)-phenyl]-ethanol hydrochloride

Aldehyde used: 2-morpholino-benzaldehyde

Yield: 0.025 g (28% of the theoretical)

k. 2-[5-amino-2-(4-dimethylamino-benzylamino)-phenyl]-ethanol and 2-[6-amino-3-(4-dimethylamino-benzylamino)-phenyl]-ethanol

Aldehyde used: 4-dimethylamino-benzaldehyde

Yield: 0.025 g (42% of the theoretical)

l. 2-[2-amino-5-(3,5-diamino-benzylamino)-phenyl]-ethanol hydrochloride and 2-[5-amino-2-(3,5-diamino-benzylamino)-phenyl]-ethanol hydrochloride

Aldehyde used: 3,5-diamino-benzaldehyde

Yield: 0.025 g (29% of the theoretical)

Mass spectrum: MH+ 273(100)

Examples 4 to 53: Hair Dyes

Hair dye solutions of the following composition are prepared:

1.25 mmoles	developer substance of Formula (I) of Table 1
1.25 mmoles	coupler of Table 1
1.0 g	potassium oleate (8% aqueous solution)
1.0 g	ammonia (22% aqueous solution)

1.0 g	ethanol
0.3 g	ascorbic acid
ad 100.0 g	water

Immediately before use, the above dye solution (50 g) is mixed with 50 g of a 6 percent aqueous hydrogen peroxide solution. Subsequently, the mixture is applied on bleached hair. After a period of action of 30 minutes at 40°C, the hair is rinsed with water, washed with a conventional, commercial shampoo and dried. The resulting dye means are summarized in Table 1.

Table 1:

Example No.	Developer Formula (I)	Coupler			
		I. 1,3-dihydroxy-benzene	**II.** 1,3-diamino-4-(2-hydroxy-ethoxy)-benzene sulfate	**III.** 5-amino-2-methyl-phenol	**IV.** 1-naphthol
4.	of Example 1a	brown	dark blue	purple	blue
5.	of Example 1b	dark blond	dark blue	purple	blue
6.	of Example 1c	dark blond	dark blue	purple	blue
7.	of Example 1d	gray	blue	purple	blue
8.	of Example 1e	dark blond	blue	purple	blue
9.	of Example 1f	dark blond	blue	purple	blue
10.	of Example 1g	dark blond	blue	purple	blue
11.	of Example 1h	medium blond	blue	purple	blue
12	of Example 1i	light blond	blue	purple	blue-gray

Table 1 (continuation)

Example No.	Developer of Formula (I)	Coupler			
		I. **1,3-dihydroxy-benzene**	**II.** **1,3-diamino-4-(2-hydroxy-ethoxy)-benzene sulfate**	**III.** **5-amino-2-methyl-phenol**	**IV.** **1-naphthol**
13.	of Example **1j**	blond	blue	purple	blue-gray
14.	of Example **1k**	dark blond	blue	purple	blue-gray
15.	of Example **1l**	brown	blue	purple-blue	blue-gray
16.	of Example **1m**	dark blond	blue	dark purple	blue
17.	of Example **1n**	light blond	blue-gray	purple	purple
18.	of Example **1o**	light blond	blue	purple	blue
19.	of Example **1p**	medium blond	blue	purple	blue
20.	of Example **1q**	dark blond	blue	purple	violet

Table 1 (continuation)

Example No.	Developer of Formula (I)	Coupler			
		I. 1,3-dihydroxy-benzene	**II. 1,3-diamino-4-(2-hydroxy-ethoxy)-benzene sulfate**	**III. 5-amino-2-methyl-phenol**	**IV. 1-naphthol**
21.	of Example **1r**	light blond	blue	purple	violet
22.	of Example **1s**	light blond	blue	purple	violet
23.	of Example **1t**	light blond	blue	purple	light violet
24.	of Example **1u**	light blond	blue	purple	light violet
25.	of Example **2a**	medium blond	blue	purple	violet
26.	of Example **2b**	blond	blue	purple	violet
27.	of Example **2c**	medium blond	blue	purple	violet
28.	of Example **2d**	medium blond	blue	purple	blue

Table 1 (continuation)

Example No.	Developer of Formula (I)	Coupler			
		I. **1,3-dihydroxy-benzene**	**II.** **1,3-diamino-4-(2-hydroxy-ethoxy)-benzene sulfate**	**III.** **5-amino-2-methyl-phenol**	**IV.** **1-naphthol**
29.	of Example **2e**	medium blond	blue	purple	violet
30.	of Example **2f**	medium blond	blue	purple	violet
31.	of Example **2g**	blond	blue	purple	violet
32.	of Example **2h**	light blond	blue	purple	violet
33.	of Example **2i**	light blond	blue	purple	violet
34.	of Example **2j**	light blond	blue	purple	violet
35.	of Example **2k**	light blond	blue	purple	gray
36.	of Example **2l**	blond	blue	purple	gray-violet

Table 1 (continuation)

Example No.	Developer of Formula (I)	Coupler			
		I. 1,3-dihydroxy-benzene	**II. 1,3-diamino-4-(2-hydroxy-ethoxy)-benzene sulfate**	**III. 5-amino-2-methyl-phenol**	**IV. 1-naphthol**
37.	of Example **2m**	light blond	blue	purple	violet
38.	of Example **2n**	dark blond	blue	purple	violet
39.	of Example **2o**	light blond	blue	purple	violet
40.	of Example **2p**	light blond	blue	purple	violet
41.	of Example **2q**	light blond	blue	purple	violet
42.	of Example **3a**	medium blond	blue	purple	blue-gray
43.	of Example **3b**	light blond	blue	purple	blue
44.	of Example **3c**	dark blond	blue	purple	violet

Table 1 (continuation)

Example No.	Developer of Formula (I)	Coupler			
		I. 1,3-dihydroxy-benzene	**II. 1,3-diamino-4-(2-hydroxy-ethoxy)-benzene sulfate**	**III. 5-amino-2-methyl-phenol**	**IV. 1-naphthol**
45.	of Example **3d**	light blond	blue	purple	light blue
46.	of Example **3e**	light blond	blue	purple	violet
47.	of Example **3f**	light blond	blue	purple	violet
48.	of Example **3g**	light blond	blue	purple	light blue
49.	of Example **3h**	light blond	blue	purple	violet
50.	of Example **3i**	light blond	blue	purple	violet
51.	of Example **3j**	light blond	blue	purple	light blue
52.	of Example **3k**	light blond	blue	purple	violet
53.	of Example **3l**	light blond	blue	purple	violet

Examples 54 to 123: Hair Dyes

Hair dye solutions of the following composition are prepared:

X g	N-(benzyl)-1,4-diamino-benzene (developer E1 to E7 of Formula (I) of Table 2)
U g	Developer E8 to E15 of Table 2
Y g	Coupler K11 to K36 of Table 4
Z g	direct dye D1 to D3 of Table 3
10.0 g	potassium oleate (8% aqueous solution)
10.0 g	ammonia (22% aqueous solution)
10.0 g	ethanol
0.3 g	ascorbic acid
ad 100.0 g	water

Immediately before use, the above dye solution (30 g) is mixed with a 30 g of a 6 percent aqueous hydrogen peroxide solution. Subsequently, the mixture is applied on bleached hair. After a period of action of 30 minutes at 40°C, the hair is rinsed with water, washed with a conventional, commercial shampoo and dried. The dyeing results are summarized in Table 5.

Examples 124 to 165: Hair Dyes

Creamy dye carrier compositions of the following composition are prepared:

X g	N-(benzyl)-1,4-diamino-benzene (developer substance E1 to E7 of Formula (I) of Table 2)
U g	Developer E8 to E15 of Table 2
Y g	Coupler K11 to K36 of Table 4

Z g	direct dye D2 of Table 3
15.0 g	cetyl alcohol
0.3 g	ascorbic acid
3.5 g	sodium lauryl alcohol diglycol ether sulfate, 28% aqueous solution
3.0 g	ammonia, 22% aqueous solution
0.3 g	sodium sulfite, anlydrous
ad 100.0 g	water

Immediately before use, the above dye cream (30 g) is mixed with 30 g of a 6 percent aqueous hydrogen peroxide solution. Subsequently, the mixture is applied on hair. After a period of action of 30 minutes at 40°C, the hair is reduced with water, washed with a conventional, commercial shampoo and dried. The dyeing results are summarized in Table 6.

Table 2:

Developer	
E1	N-((3-hydroxyphenyl)methyl)-1,4-diaminobenzene hydrochloride
E2	N-((4-aminophenyl)methyl)-1,4-diaminobenzene hydrochloride
E3	N-((4-(2-hydroxyethoxy)-phenyl)methyl)-1,4-diaminobenzene hydrochloride
E4	N-((4-methoxyphenyl)methyl-1,4-diaminobenzene hydrochloride
E5	N-{4-[(4-amino-phenylamino)-methyl]-phenyl}-acetamide hydrochloride
E6	N-((4-hydroxyphenyl)-methyl)-1,4-diaminobenzene
E7	N-benzo[1,3]dioxol-5-ylmethyl-1,4-diaminobenzene hydrochloride
E8	1,4-diaminobenzene
E9	2,5-diamino-phenylethanol sulfate
E10	3-methyl-4-amino-phenol

E11	4-amino-2-aminomethyl-phenol-dihydrochloride
E12	4-amino-phenol
E13	N,N-bis(2'-hydroxyethyl)-p--phenylenediamine sulfate
E14	4,5-diamino-1-(2'-hydroxyethyl)-pyrazole sulfate
E15	2,5-diaminotoluene sulfate

Table 3:

Direct Dyes	
D1	2,6-diamino-3-((pyridine-3-yl)azo)pyridine
D2	6-chloro-2-ethylamino-4-nitrophenol
D3	2-amino-6-chloro-4-nitrophenol

Table 4:

Coupler	
K11	1,3-diaminobenzene
K12	2-amino-4-(2'-hydroxyethyl)amino-anisole sulfate
K13	1,3-diamino-4-(2'-hydroxyethoxy)benzene sulfate
K14	2,4-diamino-5-fluoro-toluene sulfate
K15	3-amino-2-methylamino-6-methoxy-pyridine
K16	3,5-diamino-2,6-dimethoxy-pyridine-dihydrochloride
K17	2,4-diamino-5-ethoxy-toluene sulfate
K18	N-(3-dimethylamino)phenylurea
K19	1,3-bis(2,4-diaminophenoxy)propane-tetrahydrochloride
K21	3-amino-phenol
K22	5-amino-2-methyl-phenol
K23	3-amino-2-chloro-6-methyl-phenol
K24	5-amino-4-fluoro-2-methyl-phenol sulfate
K25	1-naphthol
K26	1-acetoxy-2-methyl-naphthalene
K31	1,3-dihydroxy-benzene
K32	2-methyl-1,3-dihydroxy-benzene
K33	1-chloro-2,4-dihydroxy-benzene
K34	4-(2'-hydroxyethyl)amino-1,2-methylenedioxybenzene hydrochloride
K35	3,4-methylenedioxy-phenol
K36	2-amino-5-methyl-phenol

Table 5: Hair Dyes

Example No.	**54**	**55**	**56**	**57**
Dye	(amount of dye in gram)			
E1	0.25	0.20	0.20	0.20
E10	0.30			
E11		0.30		
E12			0.30	
E14				0.30
K31	0.18			0.20
K32		0.22		
K33			0.20	
K25	0.30	0.30		0.30
K26			0.35	
Dyeing Result	reddish brown	reddish brown	reddish brown	reddish brown

Table 5: (continuation)

Example No.	**58**	**59**	**60**	**61**	**62**	**63**
Dye	(amount of dye in grams)					
E1	0.35	0.25	0.3	0.10	0.10	0.15
E8				0.15		
E9					0.15	
E15						0.15
K12			0.10			
K13	0.09	0.09				
K31	0.20			0.15	0.20	0.10
K32		0.20		0.10		0.10
K33			0.20			
K21	0.05					
K22		0.05				
K23			0.05	0.10	0.10	0.10
Dyeing Result	blond	blond	blond	blond	blond	blond

Table 5: (continuation)

Example No.	**64**	**65**	**66**	**67**
Dye	(amount of dye in grams)			
E2	0.25	0.20	0.20	0.20
E10	0.30			
E11		0.30		
E12			0.30	
E14				0.30
K31	0.18			0.20
K32		0.22		
K33			0.20	
K25	0.30	0.30		0.30
K26			0.35	
Dyeing Result	reddish brown	reddish brown	reddish brown	reddish brown

Table 5: (continuation)

Example No.	68	69	70	71	72	73
Dye	(amount of dye in grams)					
E1	0.35	0.25	0.3	0.10	0.10	0.15
E8				0.15		
E9					0.15	
E15						0.15
K12			0.10			
K13	0.09	0.09				
K31	0.20			0.15	0.20	0.10
K32		0.20		0.10		0.10
K33			0.20			
K21	0.05					
K22		0.05				
K23			0.05	0.10	0.10	0.10
Dyeing Result	blond	blond	blond	blond	blond	blond

Table 5: (continuation)

Example No.	**74**	**75**	**76**	**77**
Dye	(amount of dye in grams)			
E3	0.25	0.20	0.20	0.20
E10	0.30			
E11		0.30		
E12			0.30	
E14				0.30
K31	0.18			0.20
K32		0.22		
K33			0.20	
K25	0.30	0.30		0.30
K26			0.35	
Dyeing Result	reddish brown	reddish brown	reddish brown	reddish brown

Table 5: (continuation)

Example No.	**78**	**79**	**80**	**81**	**82**	**83**
Dye	(amount of dye in grams)					
E3	0.35	0.25	0.30	0.10	0.10	0.15
E8				0.15		
E9					0.15	
E15						0.15
K12			0.10			
K13	0.09	0.09				
K31	0.20			0.15	0.20	0.10
K32		0.20		0.10		0.10
K33			0.20			
K21	0.05					
K22		0.05				
K23			0.05	0.10	0.10	0.10
Dyeing Result	blond	blond	blond	blond	blond	blond

Table 5: (continuation)

Example No.	**84**	**85**	**86**	**87**
Dye	(amount of dye in grams)			
E4	0.25	0.20	0.20	0.20
E10	0.30			
E11		0.30		
E12			0.30	
E14				0.30
K31	0.18			0.20
K32		0.22		
K33			0.20	
K25	0.30	0.30		0.30
K26			0.35	
Dyeing Result	reddish brown	reddish brown	reddish brown	reddish brown

Table 5: (continuation)

Example No.	88	89	90	91	92	93
Dye	(amount of dye in grams)					
E4	0.35	0.25	0.30	0.10	0.10	0.15
E8				0.15		
E9					0.15	
E15						0.15
K12			0.10			
K13	0.09	0.09				
K31	0.20			0.15	0.20	0.10
K32		0.20		0.10		0.10
K33			0.20			
K21	0.05					
K22		0.05				
K23			0.05	0.10	0.10	0.10
Dyeing Result	blond	blond	blond	blond	blond	blond

Table 5: (continuation)

Example No.	**94**	**95**	**96**	**97**
Dye	(amount of dye in grams)			
E5	0.25	0.20	0.20	0.20
E10	0.30			
E11		0.30		
E12			0.30	
E14				0.30
K31	0.18			0.20
K32		0.22		
K33			0.20	
K25	0.30	0.30		0.30
K26			0.35	
Dyeing Result	reddish brown	reddish brown	reddish brown	reddish brown

Table 5: (continuation)

Example No.	98	99	100	101	102	103
Dye	(amount of dye in grams)					
E5	0.35	0.25	0.30	0.10	0.10	0.15
E8				0.15		
E9					0.15	
E15						0.15
K12			0.10			
K13	0.09	0.09				
K31	0.20			0.15	0.20	0.10
K32		0.20		0.10		0.10
K33			0.20			
K21	0.05					
K22		0.05				
K23			0.05	0.10	0.10	0.10
Dyeing Result	blond	blond	blond	blond	blond	blond

Table 5: (continuation)

Example No.	104	105	106	107
Dye	(amount of dye in grams)			
E6	0.20	0.15	0.15	0.15
E10	0.30			
E11		0.30		
E12			0.30	
E14				0.30
K31	0.18			0.20
K32		0.22		
K33			0.20	
K25	0.30	0.30		0.30
K26			0.35	
Dyeing Result	reddish brown	reddish brown	reddish brown	reddish brown

Table 5: (continuation)

Example No.	**108**	**109**	**110**	**111**	**112**	**113**
Dye	(amount of dye in grams)					
E6	0.25	0.20	0.25	0.05	0.05	0.10
E8				0.15		
E9					0.15	
E15						0.15
K12			0.10			
K13	0.09	0.09				
K31	0.20			0.15	0.20	0.10
K32		0.20		0.10		0.10
K33			0.20			
K21	0.05					
K22		0.05				
K23			0.05	0.10	0.10	0.10
Dyeing Result	blond	blond	blond	blond	blond	blond

Table 5: (continuation)

Example No.	114	115	116	117
Dye	(amount of dye in grams)			
E7	0.25	0.20	0.20	0.20
E10	0.30			
E11		0.30		
E12			0.30	
E14				0.30
K31	0.18			0.20
K32		0.22		
K33			0.20	
K25	0.30	0.30		0.30
K26			0.35	
Dyeing Result	reddish brown	reddish brown	reddish brown	reddish brown

Table 5: (continuation)

Example No.	**118**	**119**	**120**	**121**	**122**	**123**
Dye	(amount of dye in grams)					
E7	0.35	0.25	0.30	0.10	0.10	0.15
E8				0.15		
E9					0.15	
E15						0.15
K12			0.10			
K13	0.09	0.09				
K31	0.20			0.15	0.20	0.10
K32		0.20		0.10		0.10
K33			0.20			
K21	0.05					
K22		0.05				
K23			0.05	0.10	0.10	0.10
Dyeing Result	blond	blond	blond	blond	blond	blond

Table 6: Hair Dyeing Agents

Example No.	**124**	**125**	**126**	**127**	**128**	**129**
Dye	(amount of dye in grams)					
E1	1.80	1.80	1.80	0.70	0.70	0.70
K12				0.10	0.10	0.10
K13	1.10	1.10	1.10			
K31	1.10	1.10	1.10	0.40	0.40	0.40
D2				0.10	0.10	0.10
K23			0.05	0.10	0.10	0.10
Dyeing Result	black	black	black	brown	brown	brown

Table 6: (continuation)

Example No.	**130**	**131**	**132**	**133**	**134**	**135**
Dye	(amount of dye in grams)					
E2	2.00	2.00	2.00	0.80	0.80	0.80
K12				0.10	0.10	0.10
K13	1.10	1.10	1.10			
K31	1.10	1.10	1.10	0.40	0.40	0.40
D2				0.10	0.10	0.10
K23			0.05	0.10	0.10	0.10
Dyeing Result	black	black	black	brown	brown	brown

Table 6: (continuation)

Example No.	**136**	**137**	**138**	**139**	**140**	**141**
Dye	(amount of dye in grams)					
E3	2.00	2.00	2.00	0.80	0.80	0.80
K12				0.10	0.10	0.10
K13	1.10	1.10	1.10			
K31	1.10	1.10	1.10	0.40	0.40	0.40
D2				0.10	0.10	0.10
K23			0.05	0.10	0.10	0.10
Dyeing Result	black	black	black	brown	brown	brown

Table 6: (continuation)

Example No.	**142**	**143**	**144**	**145**	**146**	**147**
Dye	(amount of dye in grams)					
E4	1.90	1.90	1.90	0.70	0.75	0.75
K12				0.10	0.10	0.10
K13	1.10	1.10	1.10			
K31	1.10	1.10	1.10	0.40	0.40	0.40
D2				0.10	0.10	0.10
K23			0.05	0.10	0.10	0.10
Dyeing Result	black	black	black	brown	brown	brown

Table 6: (continuation)

Example No.	148	149	150	151	152	153
Dye	(amount of dye in grams)					
E5	2.0	2.0	2.0	0.8	0.80	0.80
K12				0.10	0.10	0.10
K13	1.10	1.10	1.10			
K31	1.10	1.10	1.10	0.40	0.40	0.40
D2				0.10	0.10	0.10
K23			0.05	0.10	0.10	0.10
Dyeing Result	black	black	black	brown	brown	brown

Table 6: (continuation)

Example No.	154	155	156	157	158	159
Dye	(amount of dye in grams)					
E6	3.00	3.00	3.00	1.20	1.20	1.20
K12				0.10	0.10	0.10
K13	1.10	1.10	1.10			
K31	1.10	1.10	1.10	0.40	0.40	0.40
D2				0.10	0.10	0.10
K23			0.05	0.10	0.10	0.10
Dyeing Result	black	black	black	brown	brown	brown

Table 6: (continuation)

Example No.	**160**	**161**	**162**	**163**	**164**	**165**
Dye	(amount of dye in grams)					
E7	2.00	2.00	2.00	0.80	0.80	0.80
K12				0.10	0.10	0.10
K13	1.10	1.10	1.10			
K31	1.10	1.10	1.10	0.40	0.40	0.40
D2				0.10	0.10	0.10
K23			0.05	0.10	0.10	0.10
Dyeing Result	black	black	black	brown	brown	brown

Unless stated otherwise, all percentages in the present application are percentages by weight.